CHAPTER 1

INTRODUCTION

1.1 Background on Portland Cement

1.1.1 Definition and History of Cement

The name cement dates back to the Romans, who called concrete-like brickwork made from stones and a burnt lime binder "opus caementitium". Later, additives such as ground bricks and volcanic ash, which were mixed with burnt lime to obtain a hydraulic binder, were given the names cementum, cimentum, caement, and cement. The term cement is used today to designate many different kinds of substances that are used as binders or adhesives.

Portland cement is a hydraulic cement, i.e. when mixed with water, it sets and hardens by hydration. After hardening, it does not disintegrate in water. Modern Portland cement originated in Britain in the nineteenth century when high temperatures were first used in the preparation of cements. The name derives from the similarity in colour and appearance to Portland stone, found on the channel coast of the Portland peninsula in Dorsetshire, England *[1, 2]*. Portland cement is the cement produced in the greatest volume and is most widely used in concrete. Portland cement was originally prepared by heating a mixture of clay and chalk. The strongly cementitious calcium silicates, Ca_2SiO_4 and Ca_3SiO_5, were thus formed. Today, various raw materials are used: either chalk, limestone or gypsum as a source of lime, together with sand, clay and iron oxide *[1, 2, 3]*.

1.1.2 Manufacture of Portland Cement

In the commercial production of Portland cement, the suitably proportioned raw materials are first ground and intimately mixed, either dry or as a slurry with water. This raw mix feed is then introduced into the top, cooler end of a long rotary kiln whose axis is inclined slightly to the horizontal. The bottom end of the kiln is heated to 1300 to 1500 °C by a suitable fuel source such as coal, oil or natural gas. As the feed passes down the kiln, it gradually heats up, first losing water and carbon dioxide. Further on, reactions between the solids begin to occur and these are completed in the hottest zone where partial melting also occurs. The presence of the liquid phase greatly speeds up the reactions by acting as a medium for the transport of matter. Reactions between solids without the help of a liquid phase are slow. An oxidizing atmosphere exists in the kiln and ensures that any iron present is in the +3 oxidation state. The partially fused black lumps (hard nodules), referred to as clinker[1], are discharged from the bottom of the kiln and rapidly cooled in an air blast. The resultant clinker is then ground to the fineness required for an adequate rate of hardening by reaction with water. To control setting time and enhance strength development, gypsum dihydrate is also added during grinding. The resulting powder is the familiar Portland cement which, when mixed with water and appropriate aggregate, hydrates to form set cement or concrete *[2, 3, 4]*.

1.1.3 Aspects of the Chemistry of Portland Cement

1.1.3.1 The Cement Chemist's Notation

The conventional cement chemist's notation uses abbreviations for the most common constituents found in Portland cements. These abbreviations will also

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[1] The term "cement clinker" originates from the late eighteenth century before rotary kilns were used. In those days, the material to be burnt was formed into bricks and then burnt in an annular kiln like ordinary bricks *[1]*.

be used throughout this document and are listed in Table 1.1. As an example, the terms C_3S, Ca_3SiO_5 and $3CaO.SiO_2$ all refer to tricalcium silicate.

Table 1.1: Cement chemist's notation

Constituent	Abbreviation
calcium oxide, CaO	C
barium oxide, BaO	B
silicon dioxide, SiO_2	S
aluminum oxide, Al_2O_3	A
ferric oxide, Fe_2O_3	F
magnesium oxide, MgO	M
sulfur trioxide, SO_3	$\bar{S}$
sodium oxide, Na_2O	N
potassium oxide, K_2O	K
carbon dioxide, CO_2	$\bar{C}$
water, H_2O	H

1.1.3.2 The Chemical Composition of Portland Cement

Portland cement clinker is formed by reactions of calcium oxide and acidic components to give mainly tricalcium silicate, Ca_3SiO_5, dicalcium silicate, Ca_2SiO_4, tricalcium aluminate, $Ca_3Al_2O_6$, and the ferrite phase, "$Ca_4Al_2Fe_2O_{10}$". These primary phases contain impurities that stabilize them at high temperatures, so that decomposition or transformations do not occur at room temperature, as happen with the pure compounds. The chemical oxide composition and the major phase composition of a typical Portland cement are given in Tables 1.2 and 1.3 *[4, 5]*.

Table 1.2: Oxide composition of a typical Portland cement

Oxide	Composition (% m/m)
CaO	63
SiO_2	20
Al_2O_3	6
Fe_2O_3	3
SO_3	2
MgO	2
$K_2O + Na_2O$	1
Others	3

Table 1.3: Phase compositions of a typical Portland cement

Phase	Composition (% m/m)
$Ca_3Al_2O_3$	5-12
Ca_3SiO_5	50-70
Ca_2SiO_4	20-30
$Ca_4Al_2Fe_2O_{10}$	5-12

1.1.3.3 Formation and Properties of the Primary Phases Found in Normal Portland Cement

In cement raw mixes, the decarbonation of limestone ($CaCO_3$) to calcium oxide takes place in the temperature region 500 to 900 °C *[6]*. Differential thermal analysis studies *[7]* showed that the decarbonation of $CaCO_3$ is endothermic. The formation of dicalcium silicate (C_2S) starts taking place before decarbonation is complete. The formation of dicalcium silicate is exothermic ($-692\ J.g^{-1}$). The formation of tricalcium silicate (C_3S) is also exothermic ($-546\ J.g^{-1}$) and starts at temperatures higher than 1300 °C. The formation of tricalcium aluminate (C_3A) is endothermic ($72\ J.g^{-1}$) and occurs at approximately 1250 °C. The formation of the ferrite phase (C_4AF) is exothermic ($-97\ J.g^{-1}$).

The solid state reactions leading to the formation of the primary phases are rather complex, but a good approximation is as follows *[8]*.

$$3CaO + Al_2O_3 \rightarrow CA \rightarrow C_{12}A_7 \rightarrow C_3A \quad (1a)$$

$$2CaO + Fe_2O_3 + Al_2O_3 \rightarrow C_2F + C_3A \rightarrow C_4AF \quad (1b)$$

$$3CaO + SiO_2 \rightarrow C_2S \rightarrow (CS, C_3S_2) \rightarrow C_3S \quad (1c)$$

The Alite Phase (C_3S)

Tricalcium silicate is the compound responsible for most of the properties of Portland cement. Tricalcium silicate hardens quickly and attains a very high strength when it is finely ground and mixed with water. It is formed by chemical reaction between calcium oxide and silicon dioxide. The reaction proceeds rapidly at 1450 °C in the presence of a melt as found during Portland cement manufacture. Tricalcium silicate is stable from its incongruent melting point, 2070 °C, down to 1250 °C. It is metastable relative to dicalcium silicate and lime; in practice, its rate of decomposition below 1250 °C is slow and there is usually no problem in preserving tricalcium silicate in cement clinker at room temperature. However, Fe^{2+} ions accelerate the decomposition to dicalcium silicate *[1]*, explaining why an oxidizing atmosphere is required during clinkering and cooling. Tricalcium silicate has an orthorhombic crystal structure in that it contains isolated SiO_4^{4-} tetrahedra. It also contains free O^{2-} ions and small amounts of Al^{3+} can be incorporated into the structure *[1, 5]*.

The Belite Phase (C_2S)

Dicalcium silicate occurs in cement when an insufficient quantity of calcium oxide for the formation of tricalcium silicate is used in the clinker. It melts congruently at 2130 °C. It hardens hydraulically the same as tricalcium silicate, but at a much slower rate and with time, it attains at least the same strength. Four stable polymorphic forms of dicalcium silicate are known to exist, while the β-form is metastable at all temperatures. The γ-form virtually does not hydrate in water *[1, 4, 5]*. It has been suggested that the reactivity of the different polymorphic forms of dicalcium silicate probably will increase in the order γ-C_2S << β-C_2S < α'-C_2S *[8]*. Other authors consider the hydraulic activity of the β-, α'_L-, α'_H- and α-forms to be similar *[1]*. The sequence of phase transformations between the polymorphs of dicalcium silicate is believed to be as shown in Figure 1.1 *[9, 10]*.

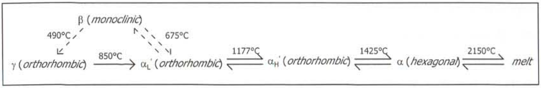

Figure 1.1: Phase transformations of dicalcium silicate

The beta to gamma transformation in dicalcium silicate is associated with a 12 % volume expansion, which explains the disintegration (dusting) sometimes experienced in clinker that is rich in dicalcium silicate *[1, 5, 9]*. Retention of the high-temperature polymorphs can be achieved by the addition of stabilizing additives or impurities *[5, 11, 12]*.

The Ferrite Phase (C_4AF)

The ferrite phase, which is often denoted by $Ca_4Al_2Fe_2O_{10}$ (C_4AF) or brownmillerite, is actually a solid solution of variable composition between $Ca_2Fe_2O_5$ (C_2F) and $Ca_2Al_2O_5$ (C_2A) *[1, 2]*. It accounts for all of the iron and part of the aluminium present in the clinker. The ferrite phase contributes very little to the hydraulic hardening process *[1, 5]*.

The Celite Phase (C_3A)

The tricalcium aluminate phase contains the aluminium oxide that is not combined in the ferrite phase. It melts incongruently, releasing calcium oxide *[1]*. Tricalcium aluminate reacts rapidly with water and although it does not have very good hydraulic properties, it improves the initial strength of cement when in combination with the calcium silicates *[1, 5]*.

1.1.3.4 Hydration of Portland Cement

In cement chemistry, the term "hydration" denotes the totality of the changes that occur when an anhydrous cement, or one of its constituent phases, is mixed with water *[5]*. The hydration of Portland cement is extremely complex and there still exist many uncertainties about some of the reactions that take place. A simplified description of the hydration reaction is as follows *[1, 4, 5]*. When water is added to Portland cement, the first compound to react is tricalcium aluminate. The C_3A is thought to dissolve very rapidly, followed by the precipitation of calcium aluminate hydrates. This reaction is accompanied by much evolution of heat. The reaction is virtually instantaneous and if nothing were added to the cement, the whole paste[2] would turn into an unworkable solid mass (flash set). In practice, flash set is avoided by adding gypsum to cement clinker. In a complex reaction, gypsum, in the presence of calcium hydroxide, acts to retard the hydration of C_3A. When gypsum is present, some of this gypsum dissolves in the water and reacts with the hydration products of the C_3A to form insoluble calcium aluminosulphates, either ettringite ($C_3A.3CaSO_4.32H_2O$) or the monosulphate ($C_3A.CaSO_4.26H_2O$). These aluminosulphates probably form a protective layer on the surface of the C_3A crystals. In this manner, the setting[3] of the cement is controlled. Ettringite is thought to form the framework in which the formation of the subsequent calcium silicate hydrate structures takes place.

Almost simultaneously with the C_3A, the C_4AF starts to hydrate, reacting with calcium hydroxide to form primarily hydrogarnet. It is generally considered that C_4AF hydration products do not materially contribute to strength development.

After C_3A and C_4AF, the next compound to hydrate is tricalcium silicate and subsequently the dicalcium silicate starts to hydrate. The slow hardening[4] and

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[2] A mixture of cement and water in such proportions that setting and hardening occur, is called a paste, the meaning of this term being extended to include the hardened material *[5]*.

[3] The term "setting" is used to denote stiffening without significant compressive strength development and usually occurs within a few hours *[5]*.

[4] The term hardening is used to indicate significant compressive strength development and is normally a slower process.

strength development of the cement is ascribed to new crystal formation and re-crystallization of the hydrated silicates from supersaturated solutions and the gradual filling of spaces in the skeleton framework by these new products thus increasing the solidity of the material.

While C_3A contributes very little to early strengths, the C_3S is the main contributor to early strengths up to seven days. At this stage, the β-C_2S also starts to react with water, which results in a continued increase in strength. The reaction products from the hydration of C_3S and β-C_2S include mainly amorphous calcium silicate hydrates, generally called C-S-H, and calcium hydroxide. In the case of C_3S hydration relatively more calcium hydroxide is formed. Simplified, the hydration reactions can be represented as follows:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad (1d)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad (1e)$$

At twenty-eight days about 70 % of the C_3S has hydrated and virtually all after one year *[5]*. Under normal conditions, the β-C_2S hydrates much slower than C_3S and after twenty-eight days only about 30 % has reacted. After one year, about 90 % of the belite has reacted *[5]*. The reaction rates depend on conditions such as particle size distribution, curing temperature and some other factors.

1.2 Considerations on the Reactivities of Clinker Phases

The ability of a substance to act as a hydraulic cement depends on its ability to react to a sufficient extent and at a sufficient rate. An understanding of the factors that control the reactivities of clinker phases is based on the knowledge of the mechanisms of their reactions with water *[5]*. The transfer of protons from the water to the solid phase is considered an essential step in these reaction mechanisms *[5]*. The solid phase thus acts as a Brønsted base. The reactivities of the oxygen atoms in the solid phases to accepting protons from the water depend on the basicities of the oxygen atoms, i.e. the magnitude of the negative charges localized on them. Any structural feature that draws electrons away from the oxygen atoms renders them less reactive, so that their basicities thus depend on the electronegativities of the atoms with which they are associated. The electronegativities of the nearest neighbours are the most important, while contributions of atoms further away also have to be considered *[5]*. This explains why C_3S, which contains some O atoms linked only to Ca, is more reactive than β-C_2S in which all the O atoms are also linked to Si. The electronegativity of Ca is 1.0 and for Si it is 1.8 *[13]*.

1.3 Stabilization of High Temperature Polymorphs of Dicalcium Silicate

As already mentioned, the high temperature polymorphs of dicalcium silicate can be chemically stabilized through addition of certain additives or "foreign" elements. When metal ions are incorporated into the lattice of β-C_2S at high temperatures, three processes can occur:

1) the cation can substitute for Si^{4+};
2) the cation can substitute for Ca^{2+};
3) the metal ion can assume an interstitial position *[12]*.

Larger charge/radius ratios will substitute for Si^{4+}, while smaller charge/radius ratios will substitute for Ca^{2+}. The introduction of stabilizing agents (usually metal oxides) into the β-C_2S lattice might produce defects that will render the C_2S highly reactive and increase the hydration rate. Increasing the stabilizing agent content will, however, not always increase the hydration rate *[12]*.

When silicon is substituted in the β-C_2S lattice, the hydration rate of the "β-C_2S" phase changes; as the charge/radius of the substituting ion increases, the hydration rate decreases (for substituting ions from V_2O_5, Cr_2O_3, B_2O_3 and SO_3). During the hydration of β-C_2S, the Si-O bonds (or M-O bonds of substituent) must be broken. Therefore, an increase in Si-O bond strength (or M-O) will decrease the hydration rate. A larger charge/radius ratio should increase the M-O bond strength, explaining why the hydration rate decreases with an increase in charge/radius ratio

[12]. As an increase in stabilizer concentration will also increase the number of stronger M-O bonds relative to Si-O bonds, the hydration rate will decrease *[12]*.

In the case of Ca^{2+} substitution, it appears that, as with silicon substitution, an increase in the charge/radius ratio will cause a decrease in the hydration rate *[12]*.

Pritts and Daugherty concluded that "reducing energy consumption in the production of Portland cement and maintaining the same cement hydration rate by increasing clinker metal doped C_2S content and reducing clinker C_3S content (everything else being held constant) is not believed to be possible" *[12]*. This statement is in contradiction to what other authors *[14, 15, 16]* have concluded more recently when they partially substituted calcium for barium. Their findings are discussed in Section 1.4.

1.4 Barium in Portland Cement

1.4.1 General Chemistry of Barium

Calcium, strontium, barium and radium form a closely allied series in which the chemical and physical properties of the elements and their compounds vary systematically with increasing size, the ionic and electropositive nature being the greatest for radium. The ionic radius of Ba^{2+} is 1.42 Å for coordination numbers of 8 and 1.61 Å for coordination numbers of 12 *[17]*. The ionic radius of calcium is 1.06 Å *[17]*.

On moving from magnesium to calcium to strontium to barium, the solubility products of MCO_3 and MSO_4 decrease. The thermal stability of MCO_3 and MSO_4 also increases from calcium to barium. The temperature at which 1 atm CO_2 dissociation pressure is reached for calcium carbonate is 900 °C, while for barium carbonate this temperature is 1360 °C. The melting points of calcium carbonate and barium carbonate are given to be approximately 2613 °C and 1923 °C respectively *[18]*.

1.4.2 Effects of Barium Additions to Portland Cement

The addition of barium to a Portland cement raw mix reduces the clinker formation temperature and improves the hydraulic properties of the belite phase *[15]*. The enthalpy of clinkerization for a barium containing raw mix is much less than for the same mix containing no barium and the clinkerization process in barium containing cement raw mixes is complete at around 1350 °C *[15]*. Clinker phases formed at lower temperatures have more "deficiencies" and are therefore more reactive *[16]*.

Barium is said to partially substitute calcium in the orthosilicates of C_2S, leading to more active orthosilicates *[16]*. This agrees with the findings of Suzuki and Yamaguchi *[14]*. Suzuki and Yamaguchi obtained the alpha-form of C_2S by stabilizing it with barium (0.15 to 0.30 mole fraction BaO substituted for CaO). Boikova et al. also found that the alpha forms of C_2S were stabilized by barium *[19]*. However, contradictory to the findings of other authors, Boikova did not find much improvement in the reactivity of C_2S *[19]*.

According to Teoreanu and Andronescu *[16]*, heating a mixture of CaO, BaO and SiO_2 in the region of 900 to 1400 °C leads to C_2S type structures. In cements where Ca^{2+} has been partially or fully replaced by Ba^{2+}, a lower lime saturation factor[5] (LSF) value is required to obtain cement with the same strength/activity as the calcium cement *[16]*. In addition, barium containing cements require more dibarium silicate and less tribarium silicate as compared to calcium cements for the same strength characteristics and, hence, lower clinkerization temperatures are required *[16]*.

In general, the rate of hydrolysis is inversely proportional to the ionic potential of Ca^{2+} and Ba^{2+} *[16]*, where the ionic potential is defined as the ratio of ionic charge to ionic radius. These values are 1.88 and 1.40 for eight-coordinated calcium and barium, respectively. It can therefore be expected that the rate of hydrolysis will increase on going from calcium-rich to barium-rich cements if the ratio of $MO:SiO_2$

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[5] See Chapter 2 for a full description of the lime saturation factor.

is the same in both cements (i.e., the same phase composition with calcium replaced by barium).

Barium hydroxide is much more soluble in water than calcium hydroxide. This may further increase the hydration rate. The solubility of $Ba(OH)_2$ in water is ≈ 60 g.ℓ^{-1} at 20 °C, while that of $Ca(OH)_2$ is only ≈ 2 g.ℓ^{-1} *[20]*.

1.5 Objectives of this Study

The ever-increasing environmental pollution and the fast depletion of fossil fuels and raw materials have all contributed to the need to find suitable ways to reduce the energy consumption in the manufacture of Portland cement. In the past few decades many improvements in the energy efficiency in Portland cement manufacture has been made, but the possibilities of further energy savings appear to be limited *[5]*.

The major component of energy consumption in the manufacture of Portland cement clinker is the decomposition of limestone ($CaCO_3$). Thus, if more of the belite phase (Ca_2SiO_4) and less of the alite phase (Ca_3SiO_5) are necessary to produce a cement of good quality, a substantial saving in the manufacturing process can be achieved. Less heat will be required and the clinkering temperature could be lowered *[15, 16, 19]*. Because of the lower lime (CaO) content required, the proportion of limestone would be reduced and consequently less carbon dioxide will be produced. It is also possible that limestone of lower purity could be used under such circumstances. In addition to these possible benefits, less calcium hydroxide will be formed during hydration of the cement, so that improved durability of products made with such cement could be expected *[11, 21]*. To allow for more belite and less alite in the cement, the reactivity of the belite phase has to be increased.

Many attempts have been made to increase the reactivity of the belite phase *[11, 21, 22]*. These attempts included stabilizing the higher temperature polymorphs (see Figure 1.1) or decreasing the crystallinity and/or the crystallite size of the belite phase. As discussed in Section 1.4, the more reactive, high temperature polymorphs of the belite phase can be chemically stabilized through the addition of small quantities of barium. Up to now most research in this regard has only been done on the system of CaO-BaO-SiO_2. However, as indicated in Section 1.1, the raw materials used in the manufacture of Portland cement also contain significant quantities of alumina and ferric oxide. It is therefore important to also have insight into the reactions of barium with silica, alumina and ferric oxide under similar reaction conditions as used for the manufacture of normal Portland cement.

This study is an attempt to obtain a better understanding of the high temperature reaction products that can be expected in systems containing combinations of BaO, Al_2O_3, Fe_2O_3 and SiO_2. In addition, the knowledge obtained in this way should be useful for evaluating some of the contradictory statements found in the literature.